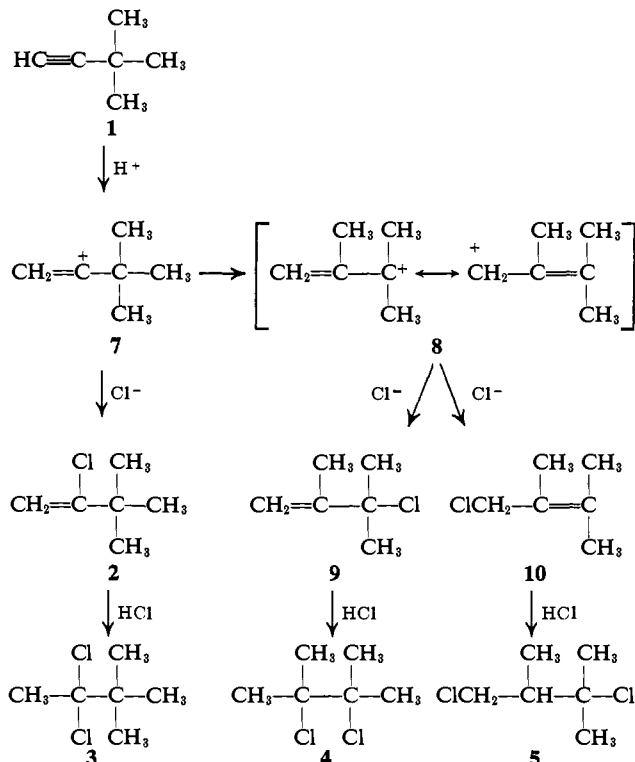


Scheme I



clarify this question, attempts are underway to assess the effect of solvent polarity upon the extent of the rearrangement.

Table I. Product Distribution in the Addition of Hydrogen Chloride to *t*-Butylacetylene

Molar ratio of HCl:1	Relative amounts of components 2-5 in crude adduct mixture, ^a mol %			
	2	3	4	5
1	42	27	5	26
5	4	44	18	34
10		36	22	42

^a The components 2-5 comprised >90% of the total adduct mixture. Minor amounts of yet unidentified by-products were formed when low ratios of HCl:1 were applied.

No evidence was obtained for the presence of 2,3-dimethylbutadiene in the crude adduct mixtures, although its formation could be envisaged by loss of a proton from **8**. Its intermediacy can, however, not be negated by this finding, since it could be shown that the reaction of excess HCl with 2,3-dimethylbutadiene, under the conditions described above, leads also predominantly to the diadduct **5** rather than **4**.⁷ The question of the intermediacy of dimethylbutadiene⁸ is, however, a secondary one as its formation would also require a 1,2-methyl shift to the vinyl cation **7**.

(7) This is quite in contrast to the previously reported reaction of aqueous HCl with 2,3-dimethylbutadiene, where the thermodynamically more stable adduct **9** was the predominant reaction product: L. F. Hatch and G. E. Journeay, *J. Amer. Chem. Soc.*, **75**, 3712 (1953).

(8) This question was raised by one of the referees and is therefore dealt with here.

K. Griesbaum, Z. Rehman

Carl Engler und Hans Bunte-Institut für Mineralöl- und Kohleforschung
Universität, 75 Karlsruhe, Germany

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Benzocyclobutene Radical Anion

Sir:

We have been studying ring strain effects on spin densities in strained aromatic radical anions.^{1,2} We wish to report some of our observations regarding the benzocyclobutene (BCB) radical anion.³

Reduction of BCB with a potassium mirror at -70° in dimethoxyethane immediately yielded the 69-line spectrum shown in Figure 1. The spectrum is readily interpreted in terms of the interaction of the electron with four sets of two equivalent nuclei. The hyperfine coupling constants are given in Table I.

Table I. Hyperfine Splitting Constants of Benzocyclobutene Radical Anion

Position	-70°	-10°	20°
Methylenes	5.20 G (2 H) 5.70 G (2 H)	5.40 G (4 H)	5.30 G (4 H)
4,5	1.45 G (2 H)	1.42 G (2 H)	1.40 G (2 H)
3,6	7.55 G (2 H)	7.28 G (2 H)	7.24 G (2 H)
Potassium		0.18 G	0.20 G

However, as the temperature was raised certain lines broadened, and when the temperature was raised to -10° the spectrum collapsed to the one shown in Figure 1. At the same time, the hyperfine coupling constants gradually changed to the values shown in Table I. One additional feature was the appearance of metal splitting at approximately -45° . The metal hyperfine splitting gradually increased as the temperature was raised. At -10° , the spectrum can be interpreted in terms of two sets of two equivalent nuclei and one set of four equivalent nuclei. We have observed this spectrum up to $+20^\circ$ and found it to be completely reversible with the low-temperature spectrum. The hyperfine coupling constants at -10° are given in Table I.

The alternating line-width effect can be associated with some exchange process. The nuclei with coupling constants of $a_H = 5.70$ G and $a_H = 5.20$ G are being interchanged and in the fast-exchange limit collapse to one set of equivalent nuclei with a splitting constant of 5.40 G. A diagram of the spin states shows that upon exchange of the quantum numbers for these two sets of nuclei all but 27 lines should broaden, as is observed. Replacement of one of the methylene protons with a deuterium yields a low-temperature spectrum which can only be simulated as a mixture of two species. The mixture was a 1:1 composition in which one species has a nucleus of splitting constant 5.20 G replaced by a deuterium atom and the second species has one of the nuclei of 5.70-G splitting constant replaced with a deuterium atom. As the temperature is raised to -10° , the spectrum collapses to one which has

(1) R. D. Rieke, C. F. Meares, and L. I. Rieke, *Tetrahedron Lett.*, 5275 (1968).

(2) R. D. Rieke, W. Rich, and T. Ridgway, *ibid.*, 4381 (1969).

(3) A preliminary report on this work was presented at the 165th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN 152.

three equivalent nuclei of splitting constant 5.40 G and one of $(2/13)5.40$ G. This clearly establishes the 5.20- and 5.70-G splitting constants as being those associated with the four methylene protons. Replacement of one of the protons *meta* to the four-membered ring established the 1.45-G splitting constant as being the 4 and 5 positions. The 7.55-G splitting constant can therefore be assigned to the 3 and 6 positions.

We had previously observed a marked change in reduction potentials of aromatic hydrocarbons upon the introduction of strain.^{2,3} Therefore, it seemed of interest to try to determine the reduction potential of BCB. Reduction of BCB with a dropping mercury electrode in acetonitrile with tetraethylammonium perchlorate as electrolyte indicated that the reduction potential was more cathodic than the solvent breakdown potential of -2.8 V *vs.* aqueous sce.⁴ The reduction potential was determined to be within a certain range of values by adding BCB radical anion to various hydrocarbons and noting when electron transfer was observed.⁵ Addition of benzene to BCB⁻ did not result in electron transfer. However, addition of biphenyl to BCB⁻ resulted in immediate transfer of electrons to form the biphenyl radical anion. Thus the reduction potential of BCB, even after it was reduced, was greater than that of biphenyl or -2.70 V.⁷ In contrast *o*-xylylene, which has its lowest vacant HMO at $E = \alpha - 0.29\beta$, is predicted to have a reduction potential of approximately -1.50 V.⁷

Further evidence that the four-membered ring remained intact was obtained from the reduction of α, α' -dibromo-*o*-xylene (I). The dibromide I was reduced with potassium under a variety of conditions in DME and diglyme. A complex 80-line signal was observed;⁸ however, it contained no sign of BCB radical anion.⁹ In addition, I was reduced exhaustively *in situ* in an epr cavity with a mercury electrode with no sign of any paramagnetic species.

Sample tubes of the BCB radical anion which had remained in contact with excess potassium at -78° for periods of time up to 8 weeks were analyzed for the parent hydrocarbon. The tubes, which had intense BCB⁻ signals, were broken open, dry air bubbled through to remove excess electrons, and analyzed by gas chromatography. The tubes which had been in contact with the excess metal for periods of 8 weeks still contained all the BCB within experimental error.

Two possibilities exist for the origin of the nonequivalency of the methylene protons. The association of the BCB radical anion with the metal cation could produce this effect.^{10,11} The existence of an equilibrium

(4) R. D. Rieke and W. Rich, unpublished results.

(5) It has been suggested that upon reduction benzocyclobutene undergoes an electrocyclic ring opening of the fused, four-membered ring to give the *o*-xylylene radical anion.⁶ Part of the driving force for this reaction was stated as being the low reduction potential of *o*-xylylene.

(6) N. Bauld and F. Farr, *J. Amer. Chem. Soc.*, **91**, 2788 (1969).

(7) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961.

(8) R. D. Rieke and S. Bales, to be published.

(9) Reduction of 2,3-bis(bromomethyl)naphthalene with a potassium mirror in glyme at -78° yielded what appeared to be an almost quantitative conversion to the radical anion of 2,3-dimethylnaphthalene.⁸ No sign of the radical anion of naphtho[b]cyclobutene was evident.¹

(10) Line-width alternation and nonequivalency of methylene protons due to ion pairing has been observed in the case of the pyraene radical anion.¹¹

(11) E. DeBoer and E. L. Mackor, *J. Amer. Chem. Soc.*, **86**, 1513 (1964).

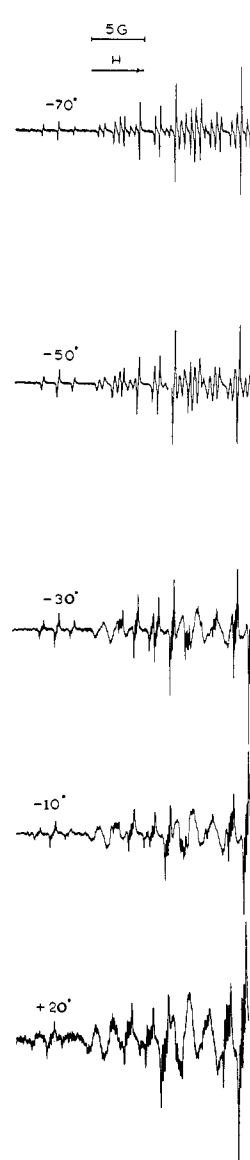


Figure 1. ESR spectra of benzocyclobutene radical anion in DME at various temperatures. The benzocyclobutene concentration was of the order of 10^{-2} M. The spectrometer gain and modulation amplitude were not kept constant. Therefore, these spectra do not show the changes in relative intensity as a function of temperature.

between a tight and loose ion pair, with the tight ion pair being favored at high temperatures, would explain the temperature dependency of the metal hyperfine splitting constant.¹² The alternating line-width effect could be the result of a dynamical equilibrium between two possible conformations.¹⁶ When the lifetime τ of a distinct conformation is short compared to $[\gamma(a_{\alpha,1} - a_{\alpha,2})]^{-1}$, in which γ is the gyromagnetic ratio of the electron, an average splitting constant for the methylene

(12) The existence of tight and loose ion pairs has been clearly established.¹³⁻¹⁵ It appears that a rapid equilibrium exists between these two types of ions and their measured epr properties depend on the equilibrium constant.

(13) R. C. Roberts and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 5542 (1965); C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *ibid.*, **87**, 5548 (1965).

(14) N. Hirota and R. Kreilick, *ibid.*, **88**, 614 (1966).

(15) T. E. Hogen-Esch and J. Smid, *ibid.*, **87**, 669 (1965).

(16) There exist several different types of ion pairs which have two conformations and would result in the methylene protons being divided into two sets of two. We have no way of distinguishing between these possibilities at the present.

protons will be observed. When the lifetime is long compared to this quantity, the epr spectrum is that of one conformation. In the intermediate case, alternating line widths result. The fact that the metal hyperfine splitting remains unbroadened as the temperature is raised suggests that the exchange process is intramolecular rather than intermolecular.

An alternate explanation for the nonequivalency of the four methylene protons is that the four-membered ring is skewed. However, we have found that when BCB is reduced in dimethoxyethane (90%) and hexamethylphosphoramide (10%) or in dimethoxyethane with crown ether the four methylene protons are equivalent even at -95° . This evidence strongly supports the thesis that the four-membered ring is still intact after reduction and the nonequivalency is caused by ion pairing.

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(17) National Defense Education Act Fellow, 1968–present.

(18) National Science Foundation Undergraduate Research Participant, 1967–1968.

R. D. Rieke, S. E. Bales,¹⁷ P. M. Hudnall, C. F. Meares¹⁸

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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Mass Spectral Rearrangements.

A Silyl McLafferty Rearrangement

Sir:

Volatile trimethylsilyl derivatives have been a popular choice for vapor phase chromatographic separation of nonvolatile materials. This has led to extensive study of the mass spectra of these derivatives for alcohols,^{1,2} carboxylic acids,³ and other functional groups.⁴ The mass spectra of functionalized organosilicon compounds *per se* have only been slightly examined.⁵ We have observed in the mass spectrum of methyl 4-trimethylsilylbutyrate⁶ two novel intramolecular rearrangements involving the silyl center.

(1) J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967).

(2) J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **33**, 2271 (1968).

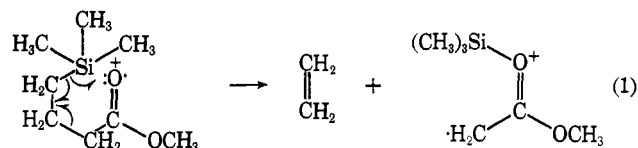
(3) J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **34**, 3147 (1969).

(4) K. M. Baker, M. A. Shaw, and D. H. Williams, *Chem. Commun.*, 1108 (1969); G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

(5) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, **91**, 6544 (1969).

(6) Methyl 4-trimethylsilylbutyrate was prepared from 3-trimethylsilylpropanol.⁷ This was converted to the corresponding tosylate. The tosylate was converted to 4-trimethylsilylbutyronitrile⁸ by treatment with sodium cyanide in DMSO. The nitrile was hydrolyzed to the corresponding methyl ester by treatment with methanolic HCl. Ir, nmr, and analytical data were in agreement with this structure. Methyl 4-trimethylsilyl-2,2-dideuteriobutyrate was prepared by reduction of methyl 3-trimethylsilylpropionate⁹ with LiAlD₄ in anhydrous ether yielding 1,1-dideuterio-3-trimethylsilylpropanol.⁷ This alcohol was converted to the desired ester *via* the tosylate and nitrile as above. Methyl-*d*₃ 4-trimethyl-silylbutyrate was prepared from 4-trimethylsilylbutyric acid¹⁰ which was converted to the corresponding acid chloride¹¹

The peak at *m/e* 146 in the mass spectrum of methyl 4-trimethylsilylbutyrate results from migration of the trimethylsilyl group from the γ carbon of the alkyl chain to the positively charged carbonyl oxygen of the ester functionality with simultaneous loss of ethylene (eq 1).



This rearrangement is similar to the McLafferty rearrangement of methyl esters,¹² with the notable difference that a trimethylsilyl group is transferred rather than a hydrogen. By comparison, alkyl groups are not normally transferred from the γ carbon to the carbonyl oxygen *via* the McLafferty rearrangement. This rearrangement is particularly unusual in that a similar photochemical rearrangement of a trimethylsilyl group from carbon to oxygen does not occur on photolysis of 5-trimethylsilyl-2-pentanone.¹³ Hence, although the normal mass spectral McLafferty rearrangement of esters is related to the photochemical Norrish type II cleavage of ketones, the silyl McLafferty rearrangement finds no analogy in a photochemical silyl Norrish type II cleavage¹³ (eq 2).

The base peak in the mass spectrum of methyl 4-trimethylsilylbutyrate is at *m/e* 73. This is due to the trimethylsilyl siliconium ion, while the peak at *m/e* 159 results from loss of a methyl group from the parent ion. Fragmentation at such a highly branched center producing these two ions is a highly favored process.^{14,15} The second most intense peak occurs at *m/e* 89. This ion is the dimethylmethoxysiliconium ion which results from migration of a methoxy group from the ester functionality to the siliconium ion center with loss of C₄H₆O, probably as ethylene and ketene. The observation of the expected metastable ion at *m/e* 49.8 (calcd 89²/159 = 49.8) provides additional evidence for this rearrangement (eq 3). This rearrangement is unimportant in the case of a similar carbonium ion¹⁶ (eq 4).

The final important rearrangement ion is the peak at *m/e* 131. This ion is most probably formed by loss of a methyl radical from the initially formed silyl McLafferty rearrangement ion *m/e* 146. The observation of the expected metastable ion at *m/e* 117.5 (calcd 131²/

with thionyl chloride. The desired ester was prepared by treatment of the acid chloride with methanol-*d*₄. The compounds so obtained agreed in physical properties with literature values and had satisfactory ir and nmr spectra. All compounds were purified by gas chromatography on a 1/4 in. \times 15 ft Carbowax 20M column before use, and were run on Varian M-66 and Perkin-Elmer Hitachi RMU-6E mass spectrometers at an ionizing voltage of 70 eV.

(7) J. L. Speier, *J. Amer. Chem. Soc.*, **74**, 1003 (1952).

(8) S. Nozakura, *Bull. Chem. Soc. Jap.*, **29**, 784 (1956).

(9) A. D. Petrov, *Zh. Obshch. Khim.*, **29**, 2936 (1959).

(10) L. H. Sommer, *J. Amer. Chem. Soc.*, **75**, 2932 (1953).

(11) L. H. Sommer, U. S. Patent No. 2,610,199; *Chem. Abstr.*, **47**, 9346 (1953).

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(16) R. Ryhage and E. Stenhagen, *Ark. Kemi*, **15**, 291 (1959); see spectrum of methyl 5-DL-methylhexacosanoate.